Sea surface temperature variations in the western Mediterranean Sea over the last 20 kyr: A dual-organic proxy (UK₃⁷ and LDI) approach

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Abstract A high-resolution sea surface temperature (SST) reconstruction of the western Mediterranean was accomplished using two independent, algae-based molecular organic proxies, i.e., the UK₃⁷ index based on long-chain unsaturated ketones and the novel long-chain diol index (LDI) based on the relative abundances of C₂₈ and C₃₀ 1,13- and 1,15-diols. Two marine records, from the western and eastern Alboran Sea basin, spanning the last 14 and 20 kyr, respectively, were studied. Results from the surface sediments suggest that the two proxies presently reflect seasons with similar SST or simply annual mean SST. Both proxy records reveal the transition from the Last Glacial Maximum to the Holocene in the eastern Alboran Sea with an SST increase of approximately 7°C for UK₃⁷ and 9°C for LDI. Minimum SSTs (10–12°C) are reached at the end of the Last Glacial Maximum and during the last Heinrich event with a subsequent rapid SST increase in LDI-SST toward the beginning of the Bölling period (20°C), while UK₃⁷-SST remains constantly low (~12°C). The Bölling-Alleröd period is characterized by a rapid increase and subsequent decrease in UK₃⁷-SST, while the LDI-SST decrease continuously. Short-term fluctuations in UK₃⁷-SST are probably related to the availability of nutrients and seasonal changes. The Younger Dryas is recorded as a short cold interval followed by progressively warmer temperatures. During the Holocene, the general lower UK₃⁷-derived temperature values in the eastern Alboran (by approximately 1.5–2°C) suggest a southeastward cold water migration by the western Alboran gyre and divergence in the haptophyte blooming season between both basins.

1. Introduction

A number of proxies are used to reconstruct past sea surface temperature (SST) changes resulting from past changes in climatic conditions. One of the earliest proxies that was developed is the stable oxygen isotopic composition of preserved carbonate shells of planktonic foraminifera [e.g., Shackleton, 1967; Erez and Luz, 1983]. The Mg/Ca ratio in foraminifera [e.g., Nürnberg et al., 1996; Elderfield and Ganssen, 2000] and the application of transfer functions and modern analog techniques (MAT) on fossil foraminiferal assemblages [e.g., Kalle et al., 1997a; González-Donoso et al., 2000; Pérez-Folgado et al., 2003; Kucera et al., 2005; Essallami et al., 2007; Sicre et al., 2013] have also been commonly used as SST proxies for paleoceanographic studies. In addition, several organic proxies have been developed for SST reconstruction [Brassell et al., 1986, Schouten et al., 2002, Rampen et al., 2012].

Long-chain alkenones (C₃₇, C₂₈, and C₃₀) were identified in marine sediments by de Leeuw et al. [1980], and Volkman et al. [1980] identified a specific group of marine phytoplankton, i.e., haptophytes (Emiliania huxleyi), as their source. Subsequently, other haptophytes, genetically closely related to E. huxleyi, were also identified as alkenone producers [e.g., Marlowe et al., 1984; Prahl and Wakeham, 1987; Conte et al., 1998]. Brassell et al. [1986] realized the potential of alkenones for reconstructing paleotemperatures and defined the UK₃⁷ index based on the relative abundances of C₃₇ di-, tri-, and tetra-unsaturated ketones, which was later simplified by exclusion of the C₃₇₄ alkenone [Prahl and Wakeham, 1987; Prahl et al., 1988]. The UK₃⁷ index is converted to SST using a global core-top calibration [Müller et al., 1998], although in some regions, such as the Mediterranean, local calibrations have been developed [Ternois et al., 1997; Conte et al., 2006]. The UK₃⁷ has been widely applied in paleoceanographic studies for at least two decades and is commonly applied on sediments spanning the last 3.5 Ma [e.g., Herbert et al., 2010].

Long-chain alkyl diols are another group of widely occurring lipids in marine sediments and are dominated by C₂₈ and C₃₀ 1,13-diols, C₂₈ and C₃₀ 1,14-diols, and C₃₀ and C₃₂ 1,15-diols [Versteegh et al., 1997]. C₂₈ and C₃₀ 1,14-diols have been identified in Proboscia diatoms [Sinninghe Damsté et al., 2003; Rampen et al., 2007] and in
the marine alga *Apedinella radians* [Rampen et al., 2011], while C_{28} and C_{30} 1,13-diols and C_{30} and C_{32} 1,15-diols have been reported in eustigmatophyte algae [Volkman et al., 1992, 1999; Gelin et al., 1997; Méjanelle et al., 2003]. However, since eustigmatophytes are not widely reported in open ocean settings, uncertainty exists about the biological source of long-chain 1,13- and 1,15-diols [Versteegh et al., 1997, 2000]. Recently, a novel long-chain diol index (LDI), based on the fractional abundances of C_{30} 1,15-diol relative to those of C_{28} 1,13-, C_{30} 1,13-, and C_{30} 1,15-diols, was proposed as a paleothermometer [Rampen et al., 2012]. In a large set of surface sediments, mainly from the North and South Atlantic Ocean, the LDI showed a strong linear correlation with SST over a temperature range of −3 to 27°C. In a marine core from the Congo River outflow, the LDI provided a SST reconstruction over the last 43 kyr, reflecting known climatic events, which was in good agreement with the U_{37}^{86}SST record [Schefuß et al., 2005; Rampen et al., 2012]. A recent study showed a LDI-reconstructed SST record off southern Australia for the last 135 kyr that generally was similar to the U_{37}^{86}, TEX_{86}, and foraminiferal assemblage SST records [Lopes dos Santos et al., 2013]. Some differences were noted in absolute SST estimates probably because the different proxies reflect SST of different seasons. Thus, the combination of diverse organic paleothermometers in marine records provides complementary information for paleoclimate and paleoceanographic reconstruction studies.

Here we present a SST reconstruction for the westernmost Mediterranean for the last 20 kyr using a dual-organic proxy approach (U_{37} and LDI). Previous SST reconstructions of the Mediterranean Sea were mainly based on U_{37} in combination with δ^{18}O values of planktonic foraminifera [e.g., Cacho et al., 1999, 2001, 2002; Emeis et al., 2000; Martrat et al., 2004, 2007]. More recently, a combination of U_{37} and TEX_{86} proxies has been applied in the western and central Mediterranean to reconstruct temperatures for the last few millennia [Grauel et al., 2013; Nieto-Moreno et al., 2013] and the penultimate interglacial to glacial cycle (from 244 to 130 kyr) [Huguet et al., 2011], and in the eastern Mediterranean for the last 30 kyr [Castañeda et al., 2010]. In general, these SST reconstructions have revealed a temperature gradient between the colder western and the warmer central Mediterranean and Levantine basin, as well as a close connection of the short-term Mediterranean climate and oceanographic variability with North Atlantic fluctuations [Cacho et al., 1999, 2001; Martrat et al., 2004, 2007; Essallami et al., 2007; Boussetta et al., 2012]. We studied two marine cores from the Alboran Sea basin to (1) obtain a continuous record of SST at high resolution for the last 20 kyr, (2) to test the relevance of the novel LDI proxy in marine records from midlatitude areas, and (3) to obtain additional information about potential seasonal effects on SST records using algae-derived organic proxies. We also discuss the response of these organic proxies on influences from the North Atlantic inflow and the specific Mediterranean thermohaline circulation in the Alboran basin.

2. Material and Methods

2.1. Study Area and Recovered Cores

The Alboran Sea basin presents a particular hydrodynamic feature, with the Atlantic jet interacting with the more saline and denser Mediterranean water. The Atlantic surface water (ASW) flows through the Strait of Gibraltar into the Alboran Sea from the west at the surface (200 m) and mixes with the Mediterranean water, forming the modified Atlantic water (MAW), flowing out the Mediterranean at depth. The ASW, which is almost homothermal (15°C), describes two near permanent anticyclonic gyres, namely, the western Alboran gyre (WAG) and the eastern Alboran gyre (EAG) [Millot, 1999], being the most characteristic features of the surface circulation in the Alboran Sea (Figure 1). Below the MAW, the Levantine intermediate waters (LIW) (200–600 m) and the deeper western Mediterranean deep water (WMDW) (>600 m) come from the east. The Mediterranean outflow water is formed through the Strait of Gibraltar, where a major proportion of LIW mixes with WMDW [Send et al., 1999] forming an outflow water mixed between eastern and western basins (Figure 1). Thus, both cores recovered are situated in a strategic position; i.e., the 434G core is located at the northern edge of the WAG and the 293G core in the transition to the EAG. These gyres show a high annual-interannual variability driven mainly by the position of the atmospheric pressure cells and the formation of high-fertility waters with enhanced production at the northern edge of the WAG [Sarhan et al., 2000].

The two analyzed gravity cores were recovered in the Alboran Sea (Figure 1). Core 293G (402 cm) was recovered from the east Alboran Sea basin (latitude: 36°10.414N, longitude: 24°51.280W; depth 1840 m below sea level (mbsl)) during the Training Through Research (TTR) 12 cruise. The inorganic geochemical, mineralogical, and grain size distribution records from this record have been reported by Rodrigo-Gámiz et al. [2011]. A
second gravity core, 434G (252.5 cm), was recovered at Ocean Drilling Program (ODP) Site 976 [Comas et al., 1996] in the west Alboran Sea basin (latitude: 36°12.313′N, longitude: 4°18.735′W; depth 1108 mbsl) during the TTR-17 (R/V Professor Logachev) cruise. The lithology of both marine sequences is dominated by homogeneous green-brownish hemipelagic mud-clays with some foraminifera and shell fragments [Comas and Ivanov, 2003].

2.2. Chronology and Oxygen Isotope Stratigraphy

The chronology of core 293G was originally established by Rodrigo-Gámiz et al. [2011] using 10 accelerator mass spectrometry (AMS) $^{14}$C dates, and two additional ones (Table 1) were obtained in order to provide a higher accuracy and robustness of critical intervals in the record. The age model of the gravity core 434G is based on linear interpolation of seven AMS radiocarbon dates of picked specimen (>125 μm; 10 mg) of the planktonic foraminifera *Globigerina bulloides*, analyzed at the Poznan Radiocarbon Laboratory (Poland) (Table 1 and Figure 2). For both cores, the radiocarbon ages were calibrated to calendar years (cal years B.P., with 0 B.P. equivalent to A.D. 1950) using Calib 6.0.2 software [Stuiver and Reimer, 1993] and the Marine09 calibration curve, with a correction for ocean surface reservoir effects of 400 years [Reimer et al., 2009], except for the time period spanning the last 17–15 kyr where a 815 year reservoir effect was applied according to Siani et al. [2001]. Similar age models were obtained using the OxCal software, but for consistency with previous studies, we used the age model obtained with the Calib software. Mean sedimentation rates obtained using these age models are 18.5 cm/kyr for core 434G (Figure 2) and 20.0 cm/kyr for core 293G [Rodrigo-Gámiz et al., 2011].

Foraminiferal stable oxygen isotope compositions ($\delta^{18}$O) in core 293G were determined on *G. bulloides* from the fraction >125 μm. The shells were analyzed using a Finnigan MAT 252 mass spectrometer with an

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Core Depth (cm)</th>
<th>Laboratory Code</th>
<th>$^{14}$C AMS Age (B.P.)</th>
<th>Calibrated Age (cal years B.P.) (Range 2σ)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>434G 0 27–28.5</td>
<td>27.75</td>
<td>Poz-40736</td>
<td>1350 ± 35</td>
<td>788–970</td>
</tr>
<tr>
<td>434G 1 30–31.5</td>
<td>66.75</td>
<td>Poz-40737</td>
<td>3350 ± 40</td>
<td>3090–3331</td>
</tr>
<tr>
<td>434G 2 18–19.5</td>
<td>108.75</td>
<td>Poz-40738</td>
<td>4680 ± 40</td>
<td>4810–5020</td>
</tr>
<tr>
<td>434G 3 27–28.5</td>
<td>175.75</td>
<td>Poz-40739</td>
<td>7960 ± 50</td>
<td>8320–8535</td>
</tr>
<tr>
<td>434G 4 15–16.5</td>
<td>217.25</td>
<td>Poz-44172</td>
<td>10,100 ± 90</td>
<td>10,762–11,244</td>
</tr>
<tr>
<td>434G 4 30–31.5</td>
<td>232.25</td>
<td>Poz-47037</td>
<td>11,140 ± 60</td>
<td>12,550–12,774</td>
</tr>
<tr>
<td>434G 4 49.5–51</td>
<td>251.75</td>
<td>Poz-37154</td>
<td>12,200 ± 70</td>
<td>13,440–13,808</td>
</tr>
<tr>
<td>293G 5 9–10.5</td>
<td>241.75</td>
<td>Poz-47104</td>
<td>10,760 ± 80</td>
<td>11,909–12,407</td>
</tr>
<tr>
<td>293G 6 30–31.5</td>
<td>320.75</td>
<td>Poz-47105</td>
<td>12,940 ± 70</td>
<td>14,219–15,110</td>
</tr>
</tbody>
</table>

*Ages were calibrated using Calib 6.0.2 software and Marine09 calibration curve (data from 2σ probability interval).
analytical reproducibility of \(< 0.07\%\) and reported in the conventional notation with reference to Vienna Pee Dee belemnite standard [see Rodrigo-Gámiz et al., 2011].

2.3. Biomarker Analysis

Core 434G was sampled continuously at 3 cm intervals and at 1.5 cm intervals for the first 16.5 cm (Late Holocene) and some critical intervals such as the Younger Dryas (YD) and Alleröd period \((n = 92)\), while core 293G was sampled each 6 cm for the time interval spanning the Holocene, and each 1.5 to 3 cm for the first 13.5 cm (Late Holocene) and the time intervals corresponding to the YD, Bölling-Alleröd (B-A) period, and the last Heinrich event (H1) \((n = 97)\).

Freeze-dried sediment samples were homogenized in agate mortar and subsequently extracted with an Accelerated Solvent Extractor (Dionex ASE 200) using a solvent mixture of 9:1 (vol/vol) dichloromethane (DCM) to methanol (MeOH) at 100°C and \(7.6 \times 10^6\) Pa. The solvent of the extract was removed by rotary evaporation. The extracts were separated into apolar, ketone, and polar fractions by column chromatography using a Pasteur pipette filled with Al\(_2\)O\(_3\) (activated for 2 h at 150°C) using 9:1 (vol/vol) hexane/DCM, 1:1 (vol/vol) hexane/DCM, and 1:1 (vol/vol) DCM/MeOH as the eluents, respectively.

2.3.1. Alkenone Analysis

The ketone fraction was dried under N\(_2\) and redissolved in a small volume (20–100 \(\mu\)L) of hexane. Quantification of the di-(\(C_{37:2}\)) and tri-unsaturated (\(C_{37:3}\)) alkenones was performed on a Hewlett Packard 6890 Gas Chromatograph (GC) using a 50 m CP Sil-5 column (0.32 mm diameter, film thickness of 0.12 \(\mu\)m), equipped with flame ionization detector and helium as the carrier gas, following GC conditions as described by Castaño et al. [2010]. Alkenone relative abundances were determined by the integration of relevant peak areas. The \(U^\prime_{37}\) index (equation (1)) was used to estimate SST [Prahl et al., 1988].

\[
U^\prime_{37} = \frac{[C_{37:2}]/([C_{37:2}] + [C_{37:3}])}
\]

\(U^\prime_{37}\) values were converted to SSTs using the global core-top calibration proposed by Müller et al. [1998]:

\[
U^\prime_{37} = 0.033 \times \text{SST} + 0.044
\]

Figure 2. Sedimentation rates along 434G sediment core calculated linearly by seven AMS \(^{14}\)C ages (open squares) calibrated with Calib 6.0.2 software [Reimer et al., 2009] (see Table 1 for details). The mean sedimentation rate of 18.5 cm/kyr is represented by dashed line.
2.3.2. Long-Chain Diol Analysis

Aliquots of the polar fractions were dried under N₂, silylated by adding 15 μL N,O-bis(trimethylsilyl) trifluoroacetamide and pyridine and heating in an oven at 60°C for 20 min, and dissolved in 50–100 μL ethyl acetate, and long-chain diols were analyzed using GC mass spectrometry as described by Rampen et al. [2012]. Different long-chain diols were quantified using selected ion monitoring of m/z 313 and 341. The long-chain diol index was calculated and converted to SST following the relation and equation by Rampen et al. [2012], which is based on more than 200 surface sediments distributed globally:

\[
LDI = \frac{[C_{30} 1, 15-diol]}{[C_{28} 1, 13-diol] + [C_{30} 1, 13-diol] + [C_{30} 1, 15-diol]} \quad (3)
\]

\[
LDI = 0.033 \times \text{SST} + 0.095 \quad (4)
\]

Replicate \((n = 29)\) and triplicate \((n = 3)\) analysis of samples from both cores showed a mean SD for the LDI of 0.02, equivalent to 0.5°C.

3. Results

For core 293G, \(^{18}\text{O}_{\text{U}^{14}\text{C}-\text{SST}}\) estimates vary between 10 (end of the Last Glacial Maximum (LGM), 17.7 cal kyr B.P.) and 20°C (Late Holocene) (Figure 3b). The B-A period shows rapid \(^{18}\text{O}_{\text{U}^{14}\text{C}-\text{SST}}\) fluctuations between 13 and 18°C in a similar pattern as observed for the \(^{18}\text{O}\) values of planktonic foraminifera (Figure 3a). The \(^{18}\text{O}_{\text{U}^{14}\text{C}-\text{SST}}\)s for
core 434G follow those observed for 293G but are approximately 2°C higher during most of the Holocene (Figure 3b).

LDI-derived SST records show a similar trend as the U\(^{37}\)\(^{37}\)-SST records (Figure 3c). For core 293G, minimum SSTs (approximately 9°C) are recorded at the end of the LGM and during H1. A marked increase is observed at the onset of the Bølling, reaching 20°C, followed by a progressive decrease during the Allerød to reach minimum SST (11°C) at the onset of the YD. From here, SST increases at a constant rate until approximately 9.7 cal kyr B.P. Subsequently, SST values remain rather stable at approximately 22°C, except for the most recent sediment horizons that reveal lower SST estimates. The LDI-SST record of core 434G shows a similar evolution with slightly lower SST values in the mid-Holocene compared to 293G (Figure 3c).

4. Discussion
4.1. Comparison of the U\(^{37}\)\(^{37}\) and LDI Proxies

Considering the calibration errors, the two proxies applied yield similar temperature estimates (~17–20°C) for the surface sediments, which are in line with annual mean but also with spring and autumn SST in the west and east Alboran basin (18.0°C–18.5°C, 17.4°C–17.8°C, and 18.0°C–18.2°C, respectively; Table 2).

In previous studies, comparison of U\(^{37}\)\(^ {37}\) temperature records with seasonal SST reconstructions based on foraminiferal fauna in the Alboran Sea have shown that the U\(^{37}\)\(^ {37}\) temperature lies close to annual mean or autumn-spring temperatures during the last 8 kyr and during the B-A period, but is higher for the LGM, suggesting that seasonal variations in alkenone production have played a role in the U\(^{37}\)\(^ {37}\) records (see Figure 1 supporting information) [Baffi et al., 2001; Pérez-Folgado et al., 2003; Essallami et al., 2007; Sicre et al., 2013]. Furthermore, fluxes of E. huxleyi and other alkenone-producing haptophytes in the Alboran Sea showed some variations over the annual cycle 1997–1998 with a minimum in winter and a maximum in May [Bártega et al., 2004]. Hence, the U\(^{37}\)\(^ {37}\)-derived SST likely represents annual mean SST with perhaps a somewhat larger influence of spring, although seasonal shifts over the last deglaciation cannot be discarded.

The strong correlation between LDI values and temperatures from the upper 30 m in the water column in globally distributed core-top sediments indicates that the photosynthetic nature of the biological source of the long-chain diols involved in the LDI [Rampen et al., 2012]. Furthermore, for the global core-top data set, the best correlation of LDI with monthly satellite SSTs was obtained for the summer-autumn season [Rampen et al., 2012]. Comparison of LDI-inferred and foraminiferal assemblage-derived SST records for the Southern Ocean suggested that the LDI reflects SST of the warmest months [Lopes dos Santos et al., 2013]. Based on this limited data, the depth habitats of alkenone and diol producers in the western Mediterranean basin are probably similar (i.e., restricted to the surface waters), although differences in the timing of seasonal production may occur. A crossplot of U\(^{37}\)\(^ {37}\) and LDI-derived SST estimates for the whole record shows that both proxies reflect, in general, similar SST estimates since the data points fall close to the 1:1 line (Figure 4) for both cores, although the somewhat lower U\(^{37}\)\(^ {37}\)-SSTs for the last 10 kyr in the 293G core clearly stand out. In general, the temperature range of the LDI-reconstructed SST over the last deglaciation (approximately 9–23°C) is slightly higher than that of U\(^{37}\)\(^ {37}\) (approximately 11–22°C), and both ranges are comparable to that reconstructed for mean annual SST based on foraminiferal assemblages (approximately 9–19°C) [Pérez-Folgado et al., 2003], although absolute values are slightly higher, suggesting that U\(^{37}\)\(^ {37}\) and LDI-reconstructed SSTs are somewhat

Table 2. Average Estimated SST (°C) Obtained for Selected Time Periods Based on Organic Proxies in Cores 434G and 293G and Present-Day Annual Mean and Seasonal Temperatures (°C) of Seawater at 0 m Depth at Both Sites Obtained From the World Ocean Atlas on a 0.25° Grid [Boyer et al., 2005]

<table>
<thead>
<tr>
<th>Time Interval</th>
<th>U(^{37})(^ {37})-SST (°C)</th>
<th>LDI-SST (°C)</th>
<th>U(^{37})(^ {37})-SST (°C)</th>
<th>LDI-SST (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core 434G</td>
<td>20.1</td>
<td>17.3</td>
<td>20.4</td>
<td>18.5</td>
</tr>
<tr>
<td>Core 293G</td>
<td>19.0 ± 0.5</td>
<td>21.2 ± 0.3</td>
<td>19.3 ± 0.3</td>
<td>21.9 ± 0.5</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>12.6 ± 0.5</td>
<td>12.4 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>19.0 ± 0.5</td>
<td>20.9 ± 0.5</td>
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<tr>
<td></td>
<td>12.6 ± 0.5</td>
<td>12.4 ± 0.5</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>18.0</td>
<td>21.3</td>
<td>18.0</td>
<td>15.4</td>
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<tr>
<td></td>
<td>15.4</td>
<td>17.4</td>
<td>18.0</td>
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</table>

\(^a^\)Equivalent to the last 30 cal years B.P. for core 434G and last 80 cal years B.P. for core 293G.
\(^b^\)Values from box core 436B (n = 39) [Nieto-Moreno et al., 2013].
\(^c^\)Standard deviation (n = 49 for U\(^{37}\)\(^ {37}\), n = 13 for LDI).
\(^d^\)Standard deviation (n = 39 for U\(^{37}\)\(^ {37}\), n = 10 for LDI).
biased to the warmer season. Differences in the stronger seasonal range in SST between the Holocene (approximately 12°C) compared to the LGM (approximately 6°C) in the Alboran Sea, as reconstructed with foraminiferal assemblage transfer functions [Pérez-Folgado et al., 2003], in combination with subtle shifts in the blooming season of alkenone and long-chain diol-producing algae may explain the differences in the $\delta^{18}O$ and LDI-SST records. Further studies on e.g., sediment traps quantifying annual fluxes of diols are needed to fully understand the possible effect of seasonality on the LDI.

A noteworthy characteristic of the Late Holocene LDI record is the decrease in reconstructed SST of approximately 4°C for the last 700 years in both cores (Figure 3c), a trend that is not seen for the $\delta^{18}O$ or foraminiferal isotope records. An identical trend was seen in the LDI in sediments recovered from a box core close to the position where core 434G was taken (data not shown). Possibly some of the long-chain diols were still present in a bound form in the most recent sediments since it is known that diols occur in eustigmatophytes in this form [Volkman et al., 1992]. However, base and acid hydrolysis of the extracts of these surface sediments resulted in the release of long-chain diols with identical LDI values as for the free diols, ruling out the possible effect of diageneis on LDI values. In good agreement with this, a similar drop in LDI values was not seen in the surface sediments from the Congo Basin [Rampen et al., 2012]. Alternatively, the main season of production of the long-chain diols has shifted over the last 700 years resulting in lower reconstructed SSTs. Clearly, more research is required to fully understand this phenomenon.

4.2. Dual-Organic Proxy Temperature Reconstruction of the Alboran Sea: Paleoceanographic Implications

The good correspondence of our $\delta^{18}O$ record of the planktonic foraminifera G. bulloides in 293G core (Figure 3a) with the stable oxygen isotope stratigraphy from Greenland ice core records (North Greenland Ice Core Project) [Lowe et al., 2008] supports our independent radiocarbon-based age model of this record. This allows to adopt the same timing and nomenclature for the climate events [see Rodrigo-Gámiz et al., 2011]. Using this framework, we will discuss the observed SST changes using the two independent organic proxies.

4.2.1. From the Last Glacial Maximum to the Deglaciation

Reconstructed SSTs using the two different proxies are approximately 14°C during the LGM (20–18 cal kyr B.P.), with absolute temperature variations of ~0.5°C for $\delta^{18}O$, while LDI-reconstructed SSTs show a larger fluctuation of ~2.5°C (Figures 3b–3c). Lowest reconstructed SSTs at 9°C and 11°C are reached at 17.8 cal kyr B.P. This decrease in SST has been previously documented by records of $\delta^{18}O$ and the Mg/Ca ratio of benthic foraminifera in the Alboran basin with reconstructed SSTs as low as ~11°C [Cacho et al., 2001, 2006; Martrat et al., 2004], around 12°C with $\delta^{18}O$ and 9–10°C with MAT in the Levantine basin (see Figure 1 supporting information) [Essallami et al., 2007; Sicre et al., 2013]. This slight increase in $\delta^{18}O$-SST along the central Mediterranean is probably related to a reduced influence of the Atlantic inflow.

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**Figure 4.** Cross correlation of LDI-SST with $\delta^{18}O$-SST for cores 293G (gray circles) and 434G (open red circles).
At the beginning of the deglaciation, H1 depicts a clear minimum in the LDI-SST record (10°C) and the oxygen isotope record but not in the \( U^{\delta^{18}O}_{37} \) record (Figure 3). This decrease in SST in the westernmost Mediterranean has been observed previously in \( U^{\delta^{18}O}_{37} \) records [Cacho et al., 1999, 2002], in a shift in planktonic \( \delta^{18}O \) values [Sierro et al., 2005; Rodrigo-Gámiz et al., 2011], by an increased relative abundance of the cold water foraminifera N. pachyderma (sinistral) [Sierro et al., 2005] and by maximum abundance of E. huxleyi shells (>4 μm) in the Alboran basin [Pérez-Folgado et al., 2003]. It is proposed to result from the inflow through the Strait of Gibraltar of colder and fresher North Atlantic water derived from the melting of icebergs [e.g., Cacho et al., 1999, 2002; Sierro et al., 2005; Rodrigo-Gámiz et al., 2011], combined with a meridional shift in the position of the polar front as suggested by other western and central Mediterranean records [e.g., Kallel et al., 1997a; Siani et al., 2001; Essallami et al., 2007; Melki et al., 2009].

At the end of the H1 event, a rapid warming trend is recorded in the LDI-SST record, reaching SSTs of 20°C at the Bölling period onset (14.7 cal kyr B.P.) (Figure 3c). A similar shift of almost 2°C is observed in the \( \delta^{18}O \) record (Figure 3a). This notable SST rise across this period has been recorded as a global warming interval preceding the Holocene using a suite of temperature proxies from a large set of SST records ([Shakun et al., 2012] and references cited therein) and is also apparent in SST data based on foraminiferal abundances in the Alboran basin [Pérez-Folgado et al., 2003]. Surprisingly, \( U^{\delta^{18}O}_{37} \)-SST remains constantly low (~12°C) during this period and only increases later (Figure 3b).

### 4.2.2. Climate Transitions in the Bölling-Alleröd and Younger Dryas

The \( U^{\delta^{18}O}_{37} \)-SST shows a rapid and abrupt SST increase from 12.5 to 18°C at the start of the Bölling and subsequently declines to SSTs of around 14°C at the end of the Alleröd (Figure 3b), while the LDI reveals a marked SST decline from 20 to 13.5°C over this period (Figure 3c). The progressive decrease in LDI-SST from the Bölling onset to the beginning of the YD in the eastern Alboran, with a shift of about 7°C, is remarkably large compared to the smaller fluctuations recorded in \( U^{\delta^{18}O}_{37} \) and, especially, \( \delta^{18}O \) (Figures 3a–3c). A previous study based on Ba/Al ratio and the presence of biogenic barite from this record revealed the occurrence of high primary productivity during H1 and the YD, while lower productivity was recorded during the B-A period [Rodrigo-Gámiz et al., 2011]. Possibly, the changing nutrient concentrations during the B-A period and transition from and to cold conditions during the H1 and YD could have induced major changes in the blooming periods of the eustigmatophyte and haptophyte algae accounting for the discongruent changes in the LDI- and \( U^{\delta^{18}O}_{37} \)-derived SST records. The effect of environmental factors like nutrient availability on the LDI still needs to be constrained [Rampen et al., 2012].

The short-term temperature fluctuations during the B-A in the \( U^{\delta^{18}O}_{37} \)-SST for eastern record are comparable with those in the \( \delta^{18}O \) profile of planktonic foraminifera (Figures 3a–3b). The availability of nutrients or oscillations in other environmental factors, causing seasonal changes in the coccolithophorid blooms in the east Alboran basin, may explain the rapid \( U^{\delta^{18}O}_{37} \)-SST fluctuations [cf. Herbert, 2003; Bárcena et al., 2004; Prahl et al., 2006]. More stable nutrient conditions in the upwelling zone in the western Alboran basin may have led to lower variability in the \( U^{\delta^{18}O}_{37} \)-SST in that area [e.g., Sarhan et al., 2000; García-Gorriz and Carr, 2001].

The late Alleröd period is documented by progressively declining SST trends in the \( U^{\delta^{18}O}_{37} \) and LDI-SST records ending at the onset of the YD (approximately 12.9 cal kyr B.P.). The SSTs reconstructed for the start of the YD with the \( U^{\delta^{18}O}_{37} \) and LDI vary in both Alboran records, i.e., 14°C and 12°C for \( U^{\delta^{18}O}_{37} \) and LDI-derived SSTs, respectively (Figures 3b–3c). This cooling event is much more pronounced than in the \( \delta^{18}O \) record (Figure 3a). In any case, the coldest phase during the YD represents a relatively short period (300–600 years), in line with other \( U^{\delta^{18}O}_{37} \) records from the western Mediterranean [Cacho et al., 2001]. The YD has been recognized in the western Mediterranean as a period that was not as cold as at higher latitudes [e.g., Maslin et al., 1995] and with an earlier warming than in Greenland [Grootes et al., 1993]. Several records from the Iberian sector and western Mediterranean region have documented the occurrence of climatic changes during the YD, pointing to an early cold/dry phase with a warmer/more humid episode during the latter phase [e.g., Combourieu Nebout et al., 2009; Naughton et al., 2007; Rodrigo-Gámiz et al., 2011]. However, in the eastern Mediterranean and northern Red Sea, organic proxies have shown a more gradual transition from the YD termination to the Holocene [Arz et al., 2003; Castañeda et al., 2010]. This coldest phase during the YD has been attributed to a southward propagation of the cold conditions throughout the Mediterranean basin [e.g., Renssen et al., 1996] with an intensification of the North Atlantic polar front by the strengthening of atmospheric cold conditions. The SST records reveal a warming from 14 to 20°C for \( U^{\delta^{18}O}_{37} \) and 12 to 19°C for LDI with slightly lower temperatures for the eastern basin.
4.2.3. Holocene SST Fluctuations and Evolution From the West to the East Alboran Basin

In general, the \( U^{37}_{37} \)-SST estimates in the western Alboran during the Holocene are similar to the alkenone record in the Gulf of Cadiz (19–22°C) [Cacho et al., 2001], while those in the eastern Alboran are in agreement with previous alkenone records and average temperatures inferred from MAT (~21°C) from nearby core sites [Cacho et al., 2001; Jiménez-Espejo et al., 2008]. The start of the Holocene (at 11,650 cal years B.P.) is recorded by a substantial SST increase of approximately 5°C until approximately 9.6 cal kyr B.P. as recorded by the LDI in both basins, mirroring the trend in the \( \delta^{18}O \) profile [Figures 3a and 3c]. In contrast, the \( U^{37}_{37} \)-SST records only reveal a slight warming of 2°C that tends to be completed earlier (approximately 10.5 cal kyr B.P.).

Another remarkable aspect is the progressive divergence in absolute SSTs derived from the \( U^{37}_{37} \)-SST index in the western and eastern Alboran basin with values of about 19–22.5°C and 18–20.5°C, respectively (Figure 3b). SST fluctuations observed in the LDI records of both western and eastern basin are larger than those for \( U^{37}_{37} \), i.e., between 16–23.5°C and 16–22.5°C, respectively (Figure 3c), but here LDI-derived SSTs from the western basin are generally lower than those from the eastern basin, a trend that is opposite from that observed for \( U^{37}_{37} \)-derived SSTs. The different responses of \( U^{37}_{37} \) between the two sites, as compared to LDI, suggest that there was more divergence in the haptophyte blooming season between both Alboran basins than for the growth season of the diol-producing algae. As mentioned before, the Alboran Sea presents a particular surface hydrological structure and circulation, with the development of the western and eastern Alboran gyres [Millot, 1999; Vargas-Yáñez et al., 2002]. The different hydrological conditions of both gyres have been previously described by particle fluxes and planktonic assemblages monitored with sediment traps during 1 year, denoting main productive events with nutrient variations and SST shifts due to the migration of both gyres during particular seasons [Sanchez-Vidal et al., 2004; Hernández-Almeida et al., 2011]. Specifically, the upwelling system located at the northern edge of WAG has undergone periodic southeastward advective displacements. In addition, major temperature anomalies, i.e., above or below the average monthly temperature, have been recorded in the Alboran basin [López García and Camarasa Belmonte, 2011]. Therefore, although the 434G core site is influenced by the superficial oceanographic circulation of the WAG and the upwelling area, this seasonal southeastward migration of colder waters to the eastern Alboran basin during late autumn and spring [Sanchez-Vidal et al., 2004] may explain the divergence in \( U^{37}_{37} \)-SSTs revealed in both Alboran basins with rapid fluctuations and lower temperatures in the eastern record. This also agrees with the indication of an eastward migration of the WAG based on SST patterns [Sánchez-Garrido et al., 2013].

The most significant Holocene cooling documented in Greenland ice core records [e.g., Alley et al., 1997], as well as in western Mediterranean cores [Cacho et al., 2001; Pérez-Folgado et al., 2003] is the 8.2 kyr event. This cooling has been previously documented through the Mediterranean areas with a drop in \( U^{37}_{37} \)-SST of 1–2°C in the Alboran Sea and a larger drop of 2.5–3°C in the Tyrrenian Sea [Cacho et al., 2001]. This short-term cooling event was also evident in the western Mediterranean with a decrease in temperate water species (Globigerinoides ruber white) and a temperature drop of around 2°C using MAT on foraminiferal assemblages [Pérez-Folgado et al., 2003]. The 8.2 kyr event is recorded at the western site with a small decrease in \( U^{37}_{37} \) and in LDI, while less evident is in \( U^{37}_{37} \) and LDI records at the eastern site (Figures 3b–3c). Overall, the general differences between \( U^{37}_{37} \) and LDI-inferred SST values during the Holocene seem to be the result of differences in the production season of alkenone and long-chain diol producers, the divergence in the haptophyte blooming season between both basins, and the particular Alboran oceanographic circulation affecting SST.

5. Conclusions

The \( U^{37}_{37} \) and LDI-SST records have yielded a high-resolution SST reconstruction for the eastern and western Alboran Sea for the past 20 and 14 kyr, respectively. These results reinforce that the LDI is indeed a suitable temperature proxy in the western Mediterranean, providing complementary information on the paleoclimate and paleoceanographic evolution. The LGM and H1 depict minima in the \( U^{37}_{37} \)-SST (12°C) and LDI-SST (10°C) records. A substantial SST increase (10°C) from H1 toward the Bölling onset is evident from the LDI-SST record, while the observed warming is more abrupt for the \( U^{37}_{37} \) and only starts in the Bölling, reaching values around 18°C. SSTs decrease during the B-A, and the first phase of the YD is recorded as a cold phase (~13°C- \( U^{37}_{37} \) and ~11°C-LDI). Early during the YD, SSTs start to rise with an overall SST increase of 5–6°C. During the Holocene, the organic proxies reflect different seasons with similar absolute SST values, ranging between 18 and 23°C, although a divergence in \( U^{37}_{37} \)-SSTs between the two basins is observed. Higher absolute
temperature values derived from $U^{13}$C in the western (19–22°C) than in the eastern site (18–20°C) suggest seasonal southeastward advective displacements of the western Alboran gyre and related cold water from the upwelling area in the southern Iberian coast and divergence in the haptophyte blooming season between both basins.

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